

SPECTROSCOPIC EVIDENCE FOR THE OCCURRENCE OF NITRATES IN LIGNITES

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INTRODUCTION

As part of a broad program of coal research at the Morgantown Coal Research Center, U.S. Bureau of Mines, extensive studies are being conducted on minerals in coal using a variety of analytical techniques. A method was successfully applied for obtaining unaltered mineral matter from coal by means of an electronic low-temperature asher (1). Significant amounts of sodium and alkaline earth nitrates were identified in lignite ashes obtained by this technique. Nitrates have not been found, however, in the ashes from any of the bituminous or anthracite coals examined to date; nitrates appear to predominate only in the ashes of lignites from the Fort Union Formation of the Great Plains coal area. These findings raised the question as to whether nitrates are formed by chemical reaction in the oxygen plasma of the asher, or are original mineral constituents of the coals. It was therefore desirable to determine, through independent methods, if nitrates are present in lignite.

This paper describes the water extraction of inorganic nitrates and their identification in the extracts by infrared spectroscopy. The presence of nitrates as original mineral constituents was confirmed, but the amount of nitrate that may have been chemically produced in the asher was not determined. The amounts of nitrates in these lignites were estimated from x-ray powder patterns of the untreated whole coals. Oxalates and sulfates were also identified by infrared spectroscopy in the water-soluble material.

EXPERIMENTAL

Coal samples were preground for 30 min. in a tungsten carbide ball mill (Spex)* and dried at 105° C for 4 hr. under a 300 ml/min. stream of nitrogen. When the moisture content is high (over about 20 pct), the coal must be predried for efficient grinding.

Infrared Spectroscopy

Pellets were prepared for infrared analysis by blending 1 mg of the sample with 500 mg of cesium iodide powder and preparing the pellet by triple pressing. The resulting pellet, 0.80 mm by 13 mm, was then scanned immediately on a Perkin-Elmer 621 infrared grating spectrophotometer purged with dry air.

* Reference to specific brands is made for identification only and does not imply endorsement by the Bureau of Mines.

Low-Temperature Oxidation

A one-gram sample of preground coal was ashed in Tracerlab's Model LTA-600L low-temperature ashers at 145° C. A stream of excited oxygen produced by a radio frequency electromagnetic field of 13.56 MHz, passed over the coal at 1 mm Hg pressure, and completely removed the organic matter in 70 to 90 hr. Temperature measurements were made with a Huggins Laboratories Mark I Infrascopes.

Water Extraction

Stepwise water extractions were conducted on three lignites. The available analytical data on the original coals are shown in Table 1. The procedure is described as follows: A preground sample of coal of known moisture content was placed in a Whatman paper Soxhlet extraction thimble between two layers of glass wool inert filler. All equipment was prewashed with distilled-deionized water. Sufficient distilled-deionized water (200 ml) was added to completely cover the sample when the thimble was placed in a 1,000 ml beaker. The sample was covered with water at all times and the water temperature was held at 90° C for 2 hr. The water solution was then removed, filtered, and carefully evaporated to dryness on a hot plate. An infrared spectrum was then obtained on this water soluble residue. The extraction was continued in this manner for a minimum of 5 to 10 separate extractions, each with a fresh volume of water as extractant. The extractions were not exhaustive or quantitative, but rather were conducted until a relatively invariant infrared spectrum was obtained.

X-ray Diffraction

Samples were mounted in 0.5 mm glass capillaries and were analyzed with iron-filtered $\text{CoK}\alpha$ radiation, using a two radian Debye-Scherrer camera for optimum resolution. The average exposure time for coal samples was 12 hr., and the use of cobalt radiation minimized the background intensity. Both low-temperature ash samples and water extraction residues provided good patterns with exposure times of 7 to 8 hr.

RESULTS AND DISCUSSION

Water Extractions

Nitrates can be water extracted from lignite only under certain conditions, and there are apparently several factors involved in a successful extraction. Several initial extraction attempts failed. For example, an extraction was attempted on the Beulah, N. D., lignite as received, with no pregrinding, and very little nitrate was extracted. Another sample of the same coal was then preground in a tungsten carbide ball mill and the identical extraction procedure repeated. Successful extraction of nitrates was then achieved and, in addition, the total material extracted was increased. Thus it became apparent that the particle size of the coal plays an important role in the nitrate extraction. For a variation in extraction technique, a 90-hr. 90° C extraction of lignite from Minot, N. D., was subsequently made in an ordinary Soxhlet apparatus, using 3.7 grams of coal and 150 ml of water. The infrared spectrum of the extract (curve a, Figure 1) showed that it

was predominantly sodium sulfate, with only a small amount of nitrates, and qualitatively very similar to the first extract from Dawson County, Mont., lignite obtained by the described extraction in a beaker after only 2 hr. (extract 1, Figure 2). It is apparent that the extraction process is not a simple function of relative solubilities, but must be a complex interplay of the ion exchange properties of the various ions present, their concentrations, and the adsorption properties of the coal substance. The salts extracted thus represent the equilibrium conditions achieved. The complexity of the system is further emphasized by the fact that sodium sulfate was not detected in the low-temperature ash from the Minot, N. D., coal, and that nitrates are generally much more soluble in water than sulfates. Sodium sulfate could not have decomposed in the low-temperature asher, as demonstrated by the fact that it is found in boiler deposits that are formed at much higher temperatures. The phenomenon responsible for the selective tenacity that the coal has for nitrates remains unexplained. One possibility is that nitrates are encapsulated in the plant structure retained by this low-rank coal. Another possibility is that nitrates are preferentially adsorbed on clays in the coal or at active sites in the coal structure. It is not known if the discrepancy between the amounts of nitrate extracted (less than 2 wt pct of the coal) and the amounts found in the low-temperature ashes is due to the production of additional nitrate during ashing.

Infrared Analysis

It was not possible to verify the presence of nitrates from infrared spectra of the coal itself because of the high background absorption of organic material. The infrared spectra of the material from five successive extraction steps for the Montana coal are shown in Figure 2. The overall spectral characteristics show that the residues are predominantly inorganic. The weak CH stretching vibrations appearing at 2850 and 2930 cm^{-1} in all extracts are assigned to fine residual coal particles which could not be filtered. Extract I is predominantly sodium sulfate, as evidenced by the strong fundamental vibration at 1128 cm^{-1} , characteristic for the sulfate ion, and the weaker bands at 990 , 628 , 612 , and 225 cm^{-1} , specific for sodium sulfate. The minor bands are unique and make possible a clear distinction between sodium sulfate and other probable sulfates such as calcium and magnesium sulfates. Sodium sulfate bands can be followed through successive extracts and are seen to gradually decrease. Also in the first extract there appears a weak but definite absorption band at 1360 cm^{-1} . The intensity of this band increases in each successive extract, as seen in Figure 2, until it becomes a major band in extract 5.

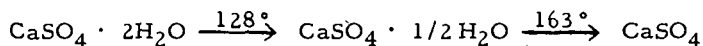
A careful study of many infrared spectral-structure correlations (2, 3, 4, 5, 6, 7) shows that there are few inorganic ions absorbing in this spectral region. Table 2 is a compilation of data from these references, showing the only possible assignments if one makes the regular assumption that the band at 1360 cm^{-1} is a characteristic group frequency, representing a class of ions. This assumption is well justified on the basis of the intensity of the band. From the data in this table and the infrared spectra of the extracts in Figure 2, a systematic elimination of all ions can be made with the exception of nitrates. For example, the nitrite ion can be readily eliminated on the basis that a strong asymmetric stretch (ν_3) for the N-O bond is required near 1260 cm^{-1} (7), and this cannot be observed in the

spectra of any of the extracts. Tetraborates, $(B_4O_7)^{2-}$, exhibiting very complex infrared spectra, require a strong absorption near 1000 cm^{-1} and metaborates, $(BO_2)^-$, require one near 950 cm^{-1} . Neither are observed in any of the spectra of the extracts.

With nitrate as the remaining possibility, the infrared spectra of a large number of inorganic nitrates were examined, both from the literature (9, 2, 10, 11, 12, 13) and from this laboratory. The absorption band observed in nearly all inorganic nitrates near 1360 cm^{-1} has been assigned to the asymmetric N-O stretching vibration (ν_3) of the nitrate ion. Its very narrow range for the inorganic class of nitrates (30 cm^{-1}) increases its specificity and usefulness. The nitrate interpretation is given additional strong support by the observation of a weak band at 825 cm^{-1} , the out-of-plane bending vibration (ν_2) for the nitrate ion, appearing well resolved in the fourth and fifth extracts, where the 1360 cm^{-1} band has become very intense. It is not possible, from the infrared spectra of these extracts alone, to establish with certainty the identity of the specific cation or cations accompanying the nitrate ion. Within nitrates as a class, the ν_2 vibration varies in position and can be used along with additional bands for a specific identification of the cation. Figure 3 presents the infrared spectra of sodium nitrate and calcium nitrate, demonstrating the relative simplicity of the infrared spectra for inorganic nitrates in general and shows the reduced intensities of additional bands. These weaker bands could not be observed in the water extracts, but in the low-temperature ashes, where nitrates appear more concentrated, all of these weaker bands have been observed.

The shoulder appearing at 1400 cm^{-1} , along with the 1360 cm^{-1} band in the water extracts, suggests the presence of alkaline earth nitrates. The splitting of the N-O stretching vibration (ν_3) into two bands for polyvalent metal nitrates and specifically for alkaline earth nitrates has been discussed by Vratny (9), Ferraro (11), and Buijs (12). This split, demonstrated in the spectrum of calcium nitrate in Figure 3, has been assigned to a reduction in symmetry and also to increasing covalent character of the nitrate ion. Infrared spectra of the low-temperature ashes give even stronger evidence for the presence of alkaline earth nitrates: The ν_3 split is observed, the ν_2 for calcium and magnesium nitrates is observed, and the bands due to water of hydration are more intense, as required for these nitrates. Carbonates in the water extracts are a possible assignment for the 1400 cm^{-1} band. However, the carbonate ν_2 out-of-plane bending in the 860 to 880 cm^{-1} region, comparable in intensity to the ν_2 for nitrates, was not observed in spectra of the extracts or in the low-temperature ashes.

As the extraction continues, the hemihydrate of calcium sulfate ($CaSO_4 \cdot 1/2H_2O$) gradually appears and can be positively identified in extract 5 by its characteristic bands at 650 and 592 cm^{-1} , as well as by the strong sulfate group vibration at 1147 cm^{-1} . The distinction between $CaSO_4$, $CaSO_4 \cdot 1/2H_2O$, and $CaSO_4 \cdot 2H_2O$ can be readily made in the infrared (1). The presence of calcium sulfate in the form of the hemihydrate indicates that the maximum temperature during evaporation of water from the extract lies between 128° and 163° C because of the following known conversions:



This indicates that the extract was not subjected to high temperatures and precludes oxidation. The position of calcium sulfate in the extraction after sodium sulfate is in line with the relative cation exchange power of calcium and sodium. Kaolinite, a clay mineral, appears in significant amounts in extracts 3 and 4 and is identified by its bands at 3695, 3620, 1100, 1030, 1010, 930, 910, 790, 750, 690, 530, 462, 425, 340, and 268 cm^{-1} . Its presence in these water extracts indicates a particle size too fine to be filtered. The strong, broad absorption bands at 3440 and 1613 cm^{-1} are vibrations assigned to water of crystallization.

The bands at 1330 and 777 cm^{-1} in this extraction were observed in the same relative intensities in all water extractions attempted, and were suspected of belonging to oxalates. Support for this interpretation was obtained from a methanol separation made on the water extract of the Minot, N. D., coal. The water extract (curve a, Figure 1) shows the suspected oxalate bands at 1330 and 777 cm^{-1} , with medium intensities. Curves (b) and (c) are the infrared spectra of the methanol soluble and methanol insoluble material, respectively. Consistent with the known insolubility of oxalates in alcohols, these bands are enhanced in the methanol insoluble material. The position and relative intensities of these two bands, along with newly resolved bands at 1640 and 507 cm^{-1} seen in curve (c) of Figure 1, are in good agreement with the infrared spectra of sodium and calcium oxalates. The observed frequencies of 1640, 1330, and 777 can be assigned to the carboxylate (O-C-O) vibrations of the asymmetric stretch (ν_9), the symmetric stretch (ν_{11}), and a deformation (ν_{12}), respectively (14). The higher solubilities of alkali oxalates compared to those of alkaline earth oxalates would support the presence of sodium oxalate in the water extracts, although increased solubilities are known when soluble oxalates combine with insoluble oxalates to form double salts. Also, calcium oxalate requires two additional medium bands at 660 and 305 cm^{-1} , which do not appear. If calcium oxalates were present in small amounts, it could be in the form of a fine particle suspension, similar to the occurrence of kaolinite in these water extracts. In view of the widespread occurrence of oxalates in plant matter, their identification in lignites is not at all unlikely.

The methanol separation shown in Figure 1 provides additional support for the presence of nitrates in lignite water extracts. As previously described, this 90-hr. Soxhlet extraction yielded only minor amounts of nitrate, as indicated by the weak absorption at 1360 cm^{-1} in curve (a). The enhancement of this band, seen in curve (b), shows that methanol has selectively dissolved nitrate, while the sodium sulfate at 1128, 990, 628, 612, and 225 cm^{-1} in curve (c) remains predominantly in the insoluble portion. This separation is in good accord with the known relative solubilities in methanol, and with methanol solubility studies on mixtures of sodium nitrate and sodium sulfate.

The stepwise extractions on the two North Dakota coals proceeded in a qualitatively similar fashion to that shown in Figure 2 for the Montana coal, achieving the same concentration of nitrate but with considerably higher amounts of oxalates. Atomic absorption analyses on the Minot, N. D., coal, both prior to and following the extraction, show that essentially all sodium was removable with distilled, demineralized water.

X-ray Analysis

X-ray powder patterns were obtained on water extracts and on the original coal samples in order to verify the presence of nitrates. Good peak-to-background ratios were obtained from the coal samples by using $\text{CoK}\alpha$ radiation (1.79 \AA), although long exposure times (12 hr.) were required. The use of radiation with shorter wavelengths (e. g. . $\text{CuK}\alpha$. 1.54 \AA) resulted in a high background, presumably because of increased Compton scattering by the organic matrix.

The interplanar spacings obtained for the Montana coal, and the ASTM data (15) for the minerals identified, are listed in Table 3. X-ray analysis of the coal samples indicated the presence of quartz, kaolinite, gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), and the nitrates of calcium and sodium. Several low-intensity lines from the ASTM data are not listed. Some kaolinite lines are absent presumably due to preferred orientation effects. The form of calcium sulfate generally occurring in coal is gypsum (1), and this is an important factor in the x-ray interpretation. Upon being subjected to low-temperature ashing or evaporation after water extraction, gypsum dehydrates to the hemihydrate. The x-ray spectral lines for the hemihydrate overlap the lines of sodium nitrate, precluding the positive identification of sodium nitrate in either the low-temperature ash or the water extract. Gypsum, however, with a completely different crystal structure, has a set of lines that do not seriously overlap those of sodium nitrate. In addition, both CaSO_4 and $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$ have specific lines that were used in determining that they were not present in the coal. As a result, the presence of sodium nitrate can be verified in the original coals, using the strong line at 3.03 \AA and the weaker line at 1.463 \AA . On the basis of the observed intensities of the sodium nitrate lines, its amount was estimated to be about 5 wt pct. The intensities of the x-ray lines were considerably greater than those for the minimum detectable amount, about 1 wt pct.

Several lines for calcium nitrate were present in the powder pattern of the Beulah, N. D., lignite and this supported the infrared evidence of alkaline earth nitrates in the water extract of this lignite. The presence of sodium oxalate could not be verified by x-ray of the lignites because all the strong lines of this compound were overlapped by those of other substances present. However, the absence of the unique lines for potassium and calcium oxalates and hydrates indicated that these particular oxalates were not present.

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TABLE 1. Lignite analyses, percent

	R. A. Newton mine, Dawson County, Mont.	Beulah, Mercer County, N. D.	Minot, Ward County, N. D.
Nitrogen	0.61	0.56	1.13
Moisture	26.2	37.6	38.4
Low-temperature ash	24.0	12.0	9.6
High-temperature ash	19.3	6.56	5.19
High-temperature ash composition:			
Na ₂ O	6.6	8.9	13.2
CaO	11.7	20.4	34.2
MgO	3.8	7.2	7.1
K ₂ O	0.8	0.4	0.75

TABLE 2. Possible polyatomic ions absorbing at 1360 cm⁻¹ *

Ion	Absorption in spectral** region of 1360 cm ⁻¹		Additional absorption bands required
	Average of range cm ⁻¹	Range cm ⁻¹	Average of range cm ⁻¹
<u>N-O Stretching Vibration</u>			
1. Nitrate, (NO ₃) ⁻	1360 (s)	30	820 (m, sharp)
2. Nitrite, (NO ₂) ⁻	1350 (w)	50	1260 (s) 800 (w)
<u>B-O Stretching Vibration</u>			
3. Tetraborate, (B ₄ O ₇) ²⁻	1400 (m-s)	110	1000 (s) 1080 (w-s)
4. Metaborate, (BO ₂) ⁻	1340 (m-s)	70	950 (s)

* Composite data from references 2 through 13.

**Intensity designations in parentheses are: s = strong, m = medium, w = weak.

TABLE 3. X-ray analysis of Dawson County, Mont., lignite

dÅ	Relative intensity*	Identification	NaNO ₃	Gypsum	Kaolinite	Quartz
7.65	M	Gypsum		7.58 ¹⁰⁰		
7.07	M	Kaolinite			7.15 ¹⁰⁰	
4.41	W	Kaolinite			4.45 ⁵⁰	
4.28	S	Gypsum, kaolinite, quartz		4.27 ⁵¹	4.35 ⁶⁰	4.26 ³⁵
4.13	W	Kaolinite			4.17 ⁶⁰ or 4.12 ³⁰	
3.83	W	NaNO ₃ , gypsum, kaolinite	3.89 ⁶	3.79 ²¹	3.84 ⁴⁰	
3.55	M	Kaolinite			3.57 ¹⁰⁰	
3.36	W	Kaolinite			3.37 ⁴⁰	
3.32	W	Quartz				3.343 ¹⁰⁰
3.26	W					
3.20	W					
3.18	W	Gypsum, kaolinite		3.163 ³	3.14 ²⁰	
3.08	M	Gypsum, kaolinite		3.059 ⁵⁷	3.09 ²⁰	
3.03	M	NaNO ₃	3.03 ¹⁰⁰			
2.97	VW					
2.85	M	NaNO ₃ , gypsum	2.81 ¹⁵	2.867 ²⁷		
2.67	M	Gypsum, kaolinite		2.679 ²⁸	2.75 ²⁰	
2.55	W	NaNO ₃ , gypsum, kaolinite	2.53 ⁹	2.591 ⁴	2.55 ⁷⁰	
2.50	W	Gypsum, kaolinite, quartz		2.495 ⁶	2.52 ⁴⁰ or 2.486 ⁸⁰	2.458 ¹²
2.32	MW	NaNO ₃ , kaolinite	2.311 ²⁴		2.374 ⁷⁰ or 2.331 ⁹⁰	

Continued

TABLE 3. X-ray analysis of Dawson County, Mont., lignite (continued)

dÅ	Relative intensity*	Identification	NaNO ₃	Gypsum	Kaolinite	Quartz
2.27	W	Kaolinite, quartz			2.284 ⁸⁰	2.282 ¹²
2.20	VW	Kaolinite, quartz			2.182 ³⁰	2.237 ⁶
2.11	W	NaNO ₃ , kaolinite, quartz	2.125 ⁹		2.127 ²⁰	2.128 ⁹
2.08	W	Gypsum		2.080 ¹⁰		
2.04	W	Gypsum, kaolinite		2.073 ⁸	2.057 ⁵	
1.98	W	NaNO ₃ , kaolinite, quartz	1.947 ⁴		1.985 ⁷⁰	1.98 ⁶
1.89	W	NaNO ₃ , gypsum, kaolinite	1.898 ¹⁶	1.898 ¹⁶	1.892 ²⁰	
1.88	W	NaNO ₃ , gypsum, kaolinite	1.880 ⁷	1.879 ¹⁰	1.865 ⁵	
1.81	W	Gypsum, kaolinite, quartz		1.812 ¹⁰	1.835 ⁴⁰	1.817 ¹⁷
1.77	W	Gypsum, kaolinite		1.778 ¹⁰	1.778 ⁶⁰	
1.66	W	NaNO ₃ , gypsum, kaolinite, quartz	1.652 ⁴	1.664 ⁴	1.682 ¹⁰	1.672 ⁷
1.61	W	NaNO ₃ , gypsum, kaolinite	1.629 ⁴	1.621 ⁶	1.616 ⁷⁰	
1.54	W	NaNO ₃ , quartz	1.544 ²			1.541 ¹⁵
1.48	W	NaNO ₃	1.463 ⁴			

* S = strong, M = medium, W = weak, V = very.

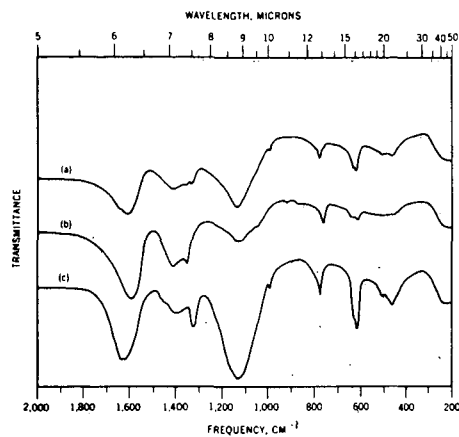


FIGURE 1. - Infrared spectra of (a) Soxhlet water extract of a North Dakota lignite; (b) methanol soluble material from (a); (c) methanol insoluble material from (a).

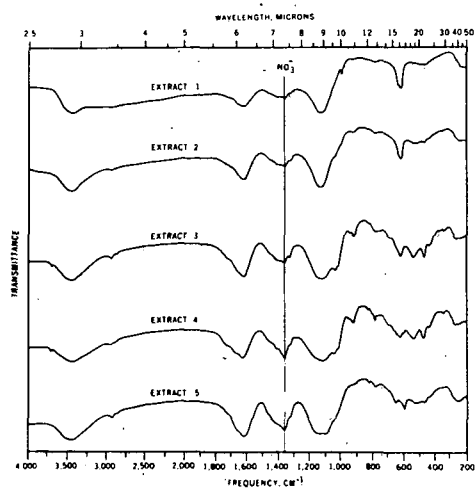


FIGURE 2. - Infrared spectra of successive water extracts from a Montana lignite.

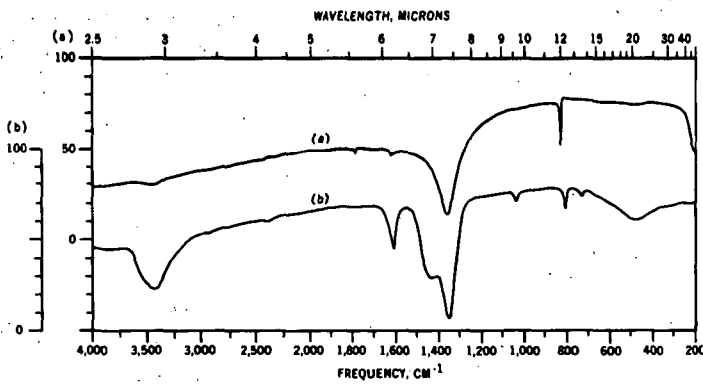


FIGURE 3. - Infrared spectra of (a) sodium nitrate, NaNO_3 ; (b) calcium nitrate, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$.